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Charge–transfer Interaction of Humic Acids with Donor Molecules in Aqueous Solutions

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Abstract. The charge–transfer acceptor properties of a humic acid in aqueous solutions have been established by spectrophotometric studies of the interactions with dihydroxobenzenes at varying pH. It is suggested that the colours of humic acids in the visible range are also dependent on internal charge–transfer interactions.

INTRODUCTION

The importance of charge–transfer interactions in humic acid chemistry does not seem to be generally appreciated by soil chemists. The possibility that charge–transfer could explain the colour of humic acids was suggested long ago (e.g. Lindqvist & Lindqvist, 1969). Ziechmann first stated the case more definitely and presented some experimental evidence for charge–transfer interactions of humic acids in organic solvents (e.g. Ziechmann, 1972, 1977). The choice of organic solvents made it possible to study many of the strongest acceptors and donors which are not soluble in aqueous solution. In our laboratory we have approached the problem in a different way by trying to establish the charge–transfer interaction in aqueous solutions. This is experimentally more difficult because of smaller concentrations and the results must be carefully evaluated in order not to draw wrong conclusions. The present results should, however, give an independent proof for the importance of charge–transfer interactions in humic acid chemistry under the conditions prevailing in soil and soil solution. In later papers results will be presented for partly reduced or oxidized and for strongly hydrolysed humic acids. The theoretical conclusions will not agree in all details with those of Ziechmann but the extreme importance of the charge–transfer interaction is completely confirmed.

EXPERIMENTAL

The soil studied was a mud-clay (Kungsängen 1 : 68, Uppsala) containing 45% (w/w) clay and 10% (w/w) organic material (determined as loss on ignition).

The humic acid was prepared in the following way: After refluxing with benzene, the humic material was extracted with 0.1 M $Na_2P_2O_7$ at pH 7. The humic acid obtained was repeatedly precipiated at pH 1 (HCl), centrifuged and redissolved at pH 7 until no precipitate could be seen after the redissolution. The pure humic acid was dialysed against distilled water and freeze-dried. The elementary composition was (in weight percentage) C: 50.1, H: 3.2, N: 2.8, O: 33.0 and ash 5.5. The fact that the sum was appreciably lower than 100% (as we had observed several times earlier) was due to the moisture which was lost before the gas chromatographic analysis (this careful study was made by Professor Wolfgang Kirsten and his collaborators). Recalculated to dry weight, the values correspond to C: 53.0, H: 3.4, N: 3.0, O: 34.9 and ash 5.8.

The freeze-dried humic acid was dissolved in buffers (standard buffers but always without borate, which reacts with the diphenols) and left over night. The solution was centrifuged at 13 200×*g* for 30 min and the decanted solution was used. There were sometimes small amounts of precipitate and therefore the following concentrations are not quite accurate. The donor molecules studied were 1,2-dihydroxybenzene (recrystallized from toluene) and 1,4-dihydroxybenzene (recrystallized from chloroform). They were dissolved in ethyl alcohol (99.5%) or water to high concentration (40%).

The alcoholic solutions were made mainly because they proved to be more stable than aqueous solutions but the same results were obtained. The effect of addition of similar amounts of ethyl alcohol or water has been shown to be negligible compared with the charge–transfer effects. New solutions were made daily. The spectrophotometric measurements were carried out in a Zeiss PM 7 spectrophotometer.

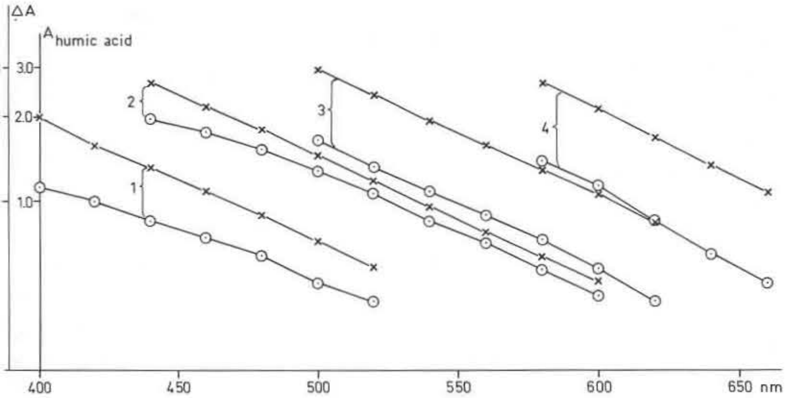

Fig. 1. Spectra of humic acid, pH 4, with 1,2-dihydroxybenzene (40% in 99,5% ethanol) at a concentration of 3.6% in the final solution. (1) 0.1% humic acid, cuvette length 0.5 cm; (2) 0.2% humic acid, cuvette length 0.5 cm; (3) 0.4% humic acid, cuvette length 0.5 cm; (4) 0.4% humic acid, cuvette length 1.0 cm. ×, humic acid; ⊙, difference.

RESULTS AND DISCUSSIONS

The shape of the charge–transfer spectra

In all cases the charge–transfer spectra developed as shoulders on the long wavelength side and not as maxima. (The shoulder has been experimentally confirmed down to 320 nm. At lower wavelengths the absorbance of the donor molecule is too strong to permit any safe determinations.) This has been observed earlier in some cases (see e.g. Briegleb et al., 1959). In Figs. 1–4 some typical charge–transfer spectra are given, together with the corresponding humic acid spectra. These experiments were carried out with 1,2-dihydroxybenzene but very similar results were obtained with 1,4-dihydroxybenzene. The examples are taken from hundreds of experiments and quite typical.

The spectroscopic effect is quite large. At the highest donor concentrations studied the increase in absorbance is of the order of 10%. The spectra are presented on a logarithmic scale in order to show the clear resemblance between the humic acid spectra and the charge–transfer spectra. This similarity is a strong indication that the spectra of the humic acids are mainly due to the same type of charge–transfer interaction as that between humic acid and the diphenols. The deviation at shorter wavelengths, where the absorbance of the humic acid changes much faster with wavelength, is easily explained as due to the aromatic character of the humic acids. The resulting spectra should thus be the sum of aromatic transitions (π–π transitions) at shorter wavelengths, with the charge–

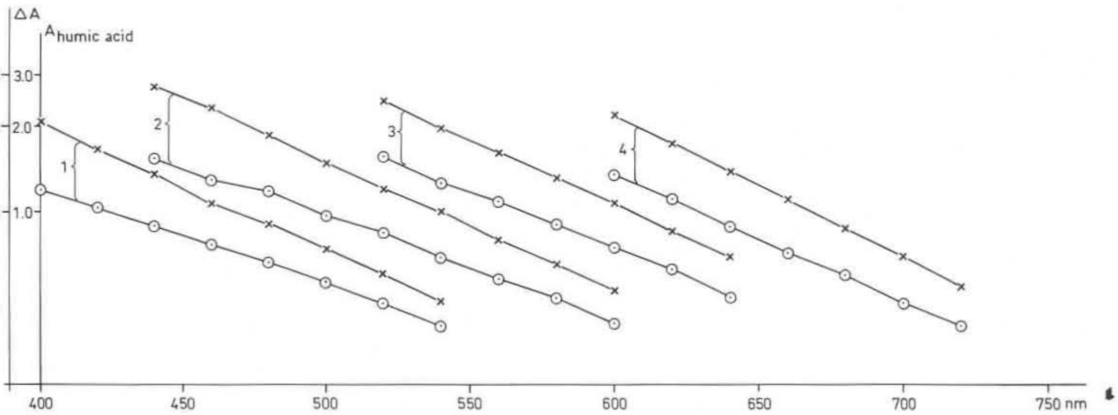

Fig. 2. Spectra of humic acid, pH 5, with 1,2-dihydroxybenzene (40% in 99.5% ethanol) at a concentration of 3.6% in the final solution. (1) 0.1% humic acid, cuvette length 0.5 cm; (2) 0.2% humic acid, cuvette length 0.5 cm; (3) 0.4% humic acid, cuvette length 0.5 cm; (4) 0.4% humic acid, cuvette length 1.0 cm. ×, humic acid; ⊙, difference.

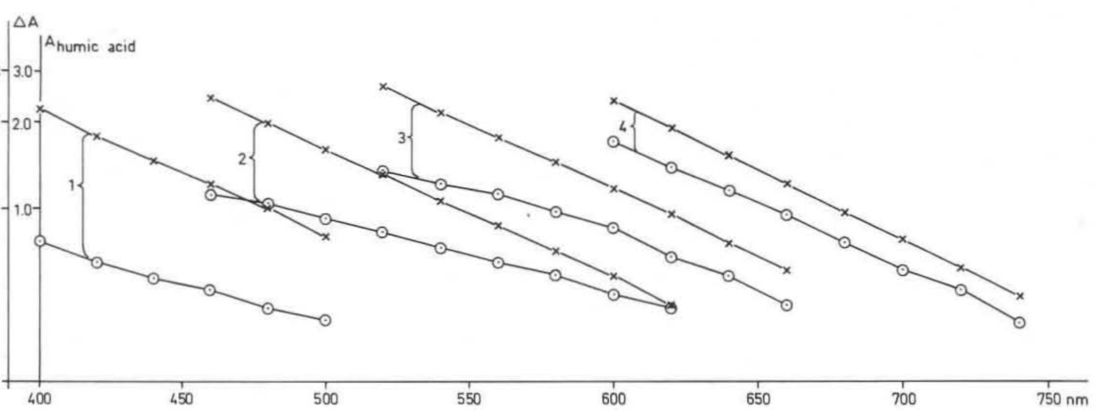

Fig. 3. Spectra of humic acid, pH 6, with 1,2-dihydroxybenzene (40% in 99.5% ethanol) at a concentration of 3.6% in the final solution. (1) 0.1% humic acid, cuvette length 0.5 cm; (2) 0.2% humic acid, cuvette length 0.5 cm; (3) 0.4% humic acid, cuvette length 0.5 cm; (4) 0.4% humic acid, cuvette length 1.0 cm. ×, humic acid; ⊙, difference.

transfer effects dominating at the longer wavelengths. We intend to make detailed studies on some other humic acids with very different absorption spectra in order to find out if the charge–transfer spectra with diphenols are also different.

One important observation must be reported in this connection. The absorbance of the humic acids cannot be explained by a simple quinhydrone reaction, because at 600 nm the absorbance is an order of magnitude larger than the absorbance of quinhydrone at the same weight concentration (these experimental results will be reported in a later paper). This large increase in absorbance is also reported in studies of the humification of the diphenols (e.g. Lindqvist & Lindqvist, 1969). Thus it remains necessary to produce a complete explanation of the high absorbance, even if charge–transfer obviously is part of the answer. Partial electron transfer might be another part.

The concentration dependence of the charge–transfer interaction

The charge–transfer absorbance increases with the product of the concentrations of humic acid and phenol. The increase is not linear, but curved as would be expected for an equilibrium reaction

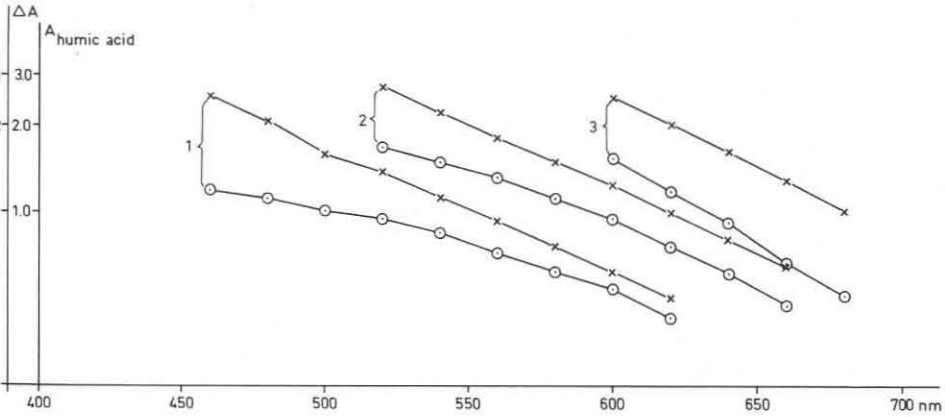

Fig. 4. Spectra of humic acid, pH 7, with 1,2-dihydroxybenzene (40% in 99.5% ethanol) at a concentration of 3.6% in the final solution. (1) 0.1% humic acid, cuvette length 1.0 cm; (2) 0.4% humic acid, cuvette length 0.5 cm; (3) 0.4% humic acid, cuvette length 1.0 cm. ×, humic acid; ⊙, difference.

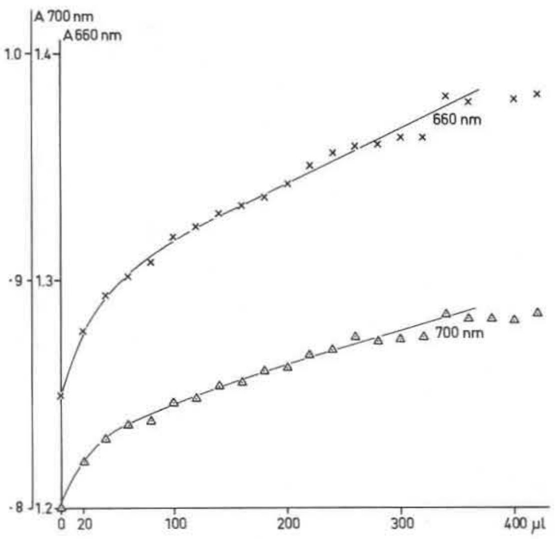

Fig. 5. Spectra of humic acid (0.4%) at pH 6 titrated with 1,2-dihydroxybenzene (40% in 99.5% ethanol) at 660 nm and 700 nm.

(Examples in Fig. 5). The results are, however, not accurate enough to permit any mathematical treatment.

The pH dependence

In Fig. 6 the variations of the difference spectra are compared with those of the humic acid spectra. The latter show a steady increase of absorbance with increasing pH, as reported earlier (e.g. Lindqvist, 1968). The small accuracy in the determination of the spectra prohibits any conclusions about variations in the pH range 3–8. There is, however, some *general effect* of pH variation which has been pointed out as typical for the humic acids (Lindqvist, 1968). There is also an obvious change at higher pH's, leading to negative difference absorbances at pH 10 and 11. This change increases with time (within an hour) indicating some kind of slow reaction. The disappearance of the direct charge–transfer addition can easily be explained by the fact that the diphenol changes to an anion (pk$_s$ 9.58) which does not react with the negatively charged humic acid anions. The negative effect is more difficult to explain. It can be a reduction, if the charge–transfer goes as far as to electron transfer and the products formed are separated in the solution.

The free radicals found in humic acids and also in the interaction with e.g. *s*-triazines and substituted ureas (Senesi, 1981) clearly indicate the occurrence of electron transfer, but it remains to define the interaction better in the case studied here.

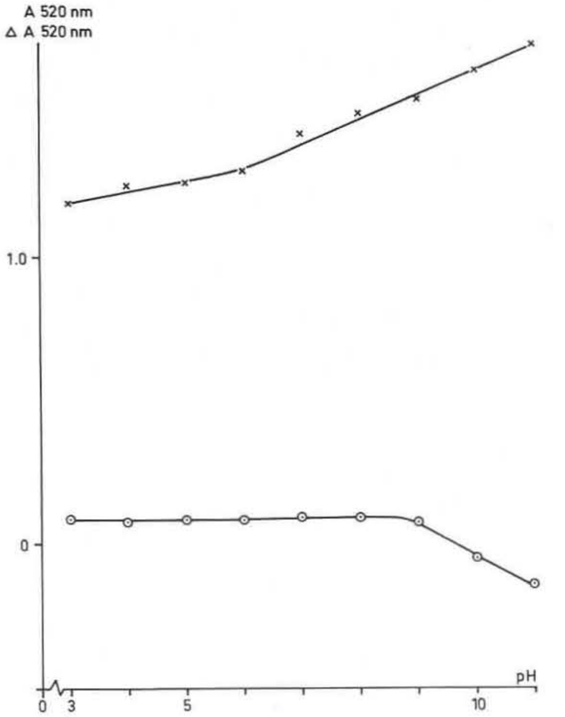

Fig. 6. Spectra for humic acid and for the difference at various pH's. 1,2-dihydroxybenzene (40% in 99.5% ethanol) is added to the amount of 3.6% in the final solutions. ×, humic acid; ⊙, difference.

At pH 13 the effect is counteracted after still longer time (about one day) by an air oxidation (or reoxidation) which again increases the absorbance. This oxidation is obtained with the diphenol alone in the buffer but it actually takes place faster (or goes further) in the presence of the humic acid. These reactions are worth studying in greater detail.

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Correction about the pH dependence

The negative effect at high pH is mainly due to the use of buffers lacking in buffer capacity. By a misunderstanding the final pH was not measured. It is obvious that the humic acid is titrated after the dihydroxybenzenes with a pk larger than 9.58.